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(54) Title: CYANINE INFRA-RED ABSORBING COMPOSITIONS AND PROCESSES FOR THE PRODUCTION THEREOF

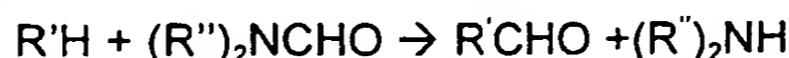
(57) Abstract: Compositions comprising cyanine infra-red absorbing compounds are provided. The compositions are substantially free from certain impurities, particularly dimethylcarbamoyl chloride. A process for the preparation of cyanine infra-red absorbing compositions is also provided.

CYANINE INFRA-RED ABSORBING COMPOSITIONS AND PROCESSES FOR THE
PRODUCTION THEREOF

This invention relates to compositions comprising cyanines, a process for making
5 the compositions and to the use of such compositions as infra-red absorbers ("IRAs").

The applicant has discovered that it is desirable to exclude certain impurities, which are volatile and highly toxic from certain cyanine compounds which can have utility as infra-red absorbers.

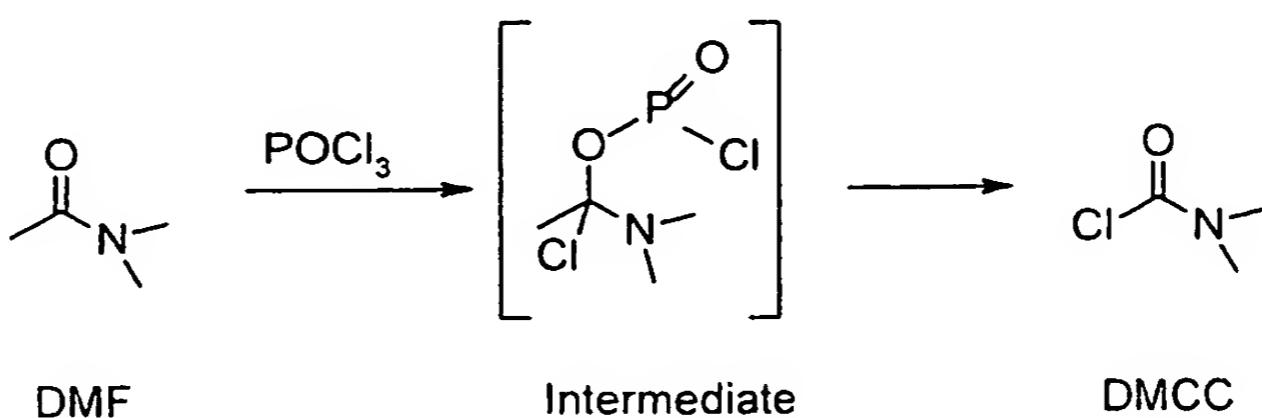
10 Cyanine compounds can be made by a synthetic route which includes preparing an intermediate using the well-known Vilsmeier Haack reaction which is shown schematically as follows:



This reaction is further described in the following references:

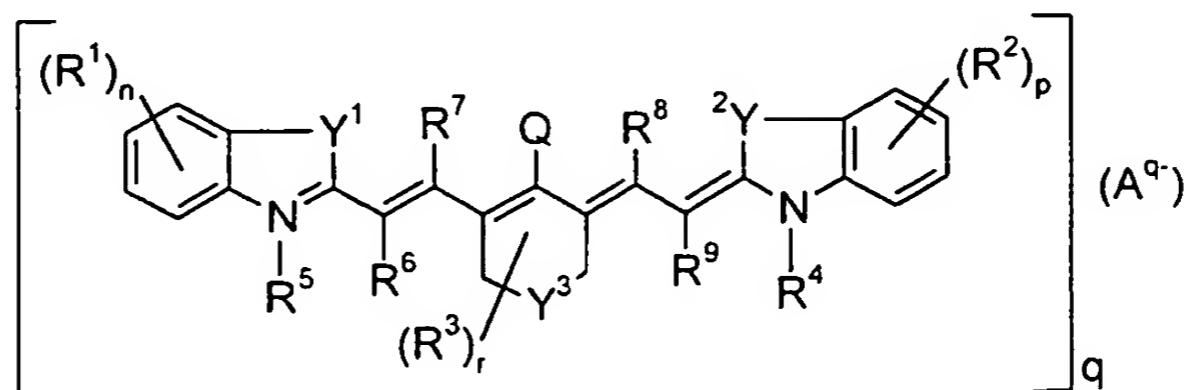
A. Vilsmeier and A. Haack, Ber. 60,119(1937); Ferguson, Chem. Revs. 38,227(1946);
15 Bosshard and Zollinger, Helv. Chim. Acta 42, 1639(1959); Maheas, Bull. Soc. Chim. France 1962,1989; G.A. Olah and S.J. Kuhn, Olah's Friedel-Crafts and Related Reactions vol 3, Part 2 (New York,1964); Jutz, Ber. 91,850(1958); Schmitt et al., Bull. Soc. Chim. France 1964,2767; and Burn et al., Tetrahedron 21,1619(1965)

20 The Vilsmeier Reaction is well known in organic synthesis and is widely used in formylation reactions. It can also be used as a method of introducing a halogen into a ring, if, for example, formylation of a cyclic ketone (such as cyclohexanone) is being undertaken. However, a common by-product of this reaction (especially when dimethyl formamide (DMF) and phosphorus oxychloride are used as the reagents) is dimethyl carbamoyl chloride (DMCC). It is believed that DMCC is formed in a side reaction of the
25 Vilsmeier Reaction (via the intermediate below).



30 The applicant has discovered that DMCC impurities and certain related impurities are highly undesirable. It is an object of the present invention to obtain useful cyanine compounds substantially free of DMCC and other similar undesirable impurities and to provide processes to achieve this.

Therefore in accordance with one aspect of the present invention there is provided a composition of matter comprising at least one compound of Formula (1) :



Formula (1)

5 where:

each R¹ to R⁹ independently represents H or an optionally substituted C₁₋₃₀hydrocarbyl group;

10 Q represents a substituent selected from substituents comprising at least one of carboxy, sulpho, hydroxy, alkoxy, aryloxy, amino, thio, mercapto, cyano, nitro and halo;

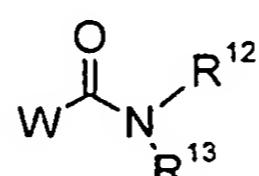
Y¹ and ²Y independently represent O, S, -NR¹⁰- and/or -C(R¹⁰)(R¹¹)-; where R¹⁰ and/or R¹¹ independently represent H or optionally substituted C₁₋₃₀hydrocarbyl;

Y³ represents -CH₂- , -CHR³- or -C(R³)₂- , or a direct bond;

A is an anion of charge (q) where q is a positive integer;

15 n, p and r are each independently 0 or an integer from 1 to 4;

characterised in that the composition is substantially free of compounds of Formula (II):



Formula (II)

20

wherein W represents an electron withdrawing substituent (such that when W is attached to an oxyphospho moiety the resultant species is stable) and R¹² and R¹³ are independently H or C₁₋₃₀hydrocarbyl, provided that neither R¹² nor R¹³ is aryl.

25 It will be recognised that when Y³ represents a direct bond between the ring atoms to which it is attached, the bridging ring of which Y³ is a part will be a five membered ring.

The compound of Formula (1) may comprise any form of the compound: such as salt, stereoisomer, zwitterion, polymorph, complex, isotopic form, combinations thereof in the same species and mixtures thereof.

One or more of the groups represented by R¹ and R² may, together with the phenyl moiety to which they are bonded, form a fused ring moiety, preferably a fused aromatic moiety such as a naphthyl moiety.

Preferably at least one of R⁴ and R⁵ is not H, and most preferably neither are H.

5 The substituent represented by Q and selected from substituents comprising at least one of carboxy, sulpho, hydroxy, alkoxy, aryloxy, amino, thio, mercapto, cyano, nitro and halo includes groups of formulae -COR, -CO₂R, CONR₂, -OR, -SR, -NR₂, -SO₂R and -SO₂NR₂, wherein each R independently is H or an alkyl or aryl group.

10 Preferably W is a halo, more preferably bromo, chloro or fluro, and most preferably chloro or bromo. Preferably the compositions of the present invention are substantially free from any dimethyl carbamoyl chloride (DMCC).

Preferably the impurity-free compositions of the present invention have utility as an infra-red absorber.

15 Preferably the compositions of the present invention are substantially free from compounds of Formula (II), and particularly DMCC, to the extent that the compositions comprise no more than about 100 ppb, more preferably no more than about 50ppb and most preferably no more than about 10ppb of compound of Formula (II) with respect to compound of Formula (1). It is especially preferred that compounds of Formula (II), particularly DMCC, are absent from compositions of the present invention (to the extent 20 that it is undetectable by any conventional analytical technique).

Preferred compounds of Formula (1) are those in which:

each R¹ to R⁹ independently represents H or optionally substituted C₁₋₁₂alkyl, provided at least one of R⁴ or R⁵ is optionally substituted C₁₋₁₂alkyl;

Q is a halo group:

25 Y¹ and ²Y are each independently selected from -C(R¹⁰)(R¹¹)-; where R¹⁰ and R¹¹ independently represent H or C₁₋₃₀hydrocarbyl;

Y³ is -CH₂- , -CHR³- or -C(R³)₂- (i.e. the bridging ring is six membered);

A is a monovalent anion;

q is 1;

30 n and p are each independently 0, or an integer from 1 to 3; and

r is 0 or an integer from 1 to 4.

More preferred compounds of Formula (1) are those preferred compounds in which:

R¹ to R⁵ are each independently selected from: optionally substituted C₁₋₄alkyl;

35 R⁶ to R⁹ are each H;

Q is Cl or Br;

Y¹ and Y² are each independently a methylene group independently optionally substituted by one or two optionally substituted C₁₋₄alkyl groups;

Y³ is methylene optionally substituted with an optionally substituted C₁₋₄alkyl;

A is halide; or an inorganic or organic sulphur-containing ion, commonly tosylate;

5 q is 1; and

n, p and r are each independently 0 or 1.

Most preferred compounds of Formula (1) are those more preferred compounds in which:

R⁴ and R⁵ are both C₁₋₄alkyl;

10 R⁶ to R⁹ are each H;

Q represents a halo group;

Y¹ and ²Y are both -C(C₁₋₄alkyl)₂-;

Y³ is methylene;

A is chloride, bromide, SbF₆⁻, PF₆⁻ or tosylate;

15 q is 1; and

n, p and r are each 0.

Specific compounds of Formula (1) comprise those compounds exemplified herein.

Optional substituents which may be present in the present invention include 20 substituents comprising a moiety selected from carboxy, -CO₂H and salts thereof, sulphonyl, -SO₃H and salts thereof, formyl, hydroxy, amino, imino, nitrilo, mercapto, cyano, nitro, halo, alkyl, preferably C₁₋₄alkyl, such as methyl and alkoxy, preferably C₁₋₄alkoxy such as methoxy; and includes direct combinations of a plurality (preferably two) of these groups (e.g. amino and sulphonyl combined are sulphamoyl; 25 carboxy and alkyl are keto; carboxy and alkoxy are ester). Particular examples of such substituents are those of formulae -COR, -CO₂R, CONR₂, OR, -SR, -NR₂, -SO₂R and -SO₂NR₂, wherein each R independently is H or an alkyl or aryl group. Preferred optional 30 substituents comprise: -SO₃H and salts thereof, hydroxy, amino, thio, cyano, halo, methyl (optionally substituted by one or more halo) and/or methoxy (optionally substituted by one or more halo).

The term 'hydrocarbyl' as used herein includes any organic radical moiety which comprises one or more hydrogen atoms and carbon atoms and optionally one or more other heteroatoms preferably selected from phosphorus, halo, nitrogen, oxygen and/or sulphur, more preferably from nitrogen, oxygen and/or sulphur, and also includes perhalogenated derivatives thereof, such as -CF₃. Most preferably hydrocarbyl moieties 35 comprise one or more of the following carbon containing moieties (including combinations thereof in the same moiety): alkyl, alkoxy, alkanoyl, aryl, aryloxy, carboxy,

and/or formyl in optional combination with one or more of the following heteroatom containing moieties (including direct combinations of a plurality (preferably two) of the heteroatom moieties, (e.g. amino and sulphanyl combined are sulphinamoyl)): oxy, thio, sulphanyl, sulphonyl, amino, imino and/or nitrilo. Hydrocarbyl moieties may also 5 comprise one or more double and/or triple carbon to carbon bonds.

Alkyl groups herein may be linear, branched or cyclic and preferably comprise up to 12 carbon atoms, and most preferably up to 6 carbon atoms, such as from 1-4 carbon atoms. Alkyl groups may be substituted or unsubstituted.

Aryl groups herein include heteraryl groups. The aryl groups may be 10 substituted or unsubstituted and may comprise two or more fused rings. The most preferred aryl group is a phenyl group.

The term 'halo' as used herein signifies fluoro, chloro, bromo or iodo, preferably chloro.

Any radical group or moiety mentioned herein (e.g. as a substituent) refers to a 15 monovalent radical unless otherwise stated or the context clearly indicates otherwise (e.g. an alkylene moiety is bivalent and links two other moieties). A group which comprises a chain of three or more atoms signifies a group in which the chain wholly or in part may be linear, branched and/or form a ring (including spiro and/or fused rings). The total number of certain atoms is specified for certain substituents for example 20 C₁₋₁₅hydrocarbyl, signifies a hydrocarbyl moiety comprising from 1 to 15 carbon atoms. In any of the formulae drawn herein if one or more ring substituents are not indicated as attached to any particular atom on the ring [for example the substituent R¹ in Formula (1)] the substituent may replace any H attached to an atom in the ring and may be located at any available position on the ring which is chemically suitable. If substituents 25 which may be attached to a ring in the Formulae herein are represented by an optional plurality of a group herein (e.g. n x R¹, p x R² and/or r x R³) different substituents may be attached to the same ring and/or to the same atom in the ring (where valence allows) such that each occurrence of a substituent (e.g. R³) may be independent of any other occurrence of the same substituent on the same ring and/or atom (e.g. R³).

30 According to a further feature of the present invention there is provided a composition effective for use as an infra-red absorber (IRA-effective) comprising a medium and an IRA-effective compound of Formula (1) as defined herein.

The term 'IRA effective' (for example with reference to the inks, compositions, ingredients, substituents and/or compounds described herein) will be understood to 35 mean effective for use as an infra-red absorber by absorbing electromagnetic radiation in the infra-red region (preferably at a wavelength of from about 640 nm to about 1,100 nm).

The compositions of the present invention are useful for absorbing electromagnetic radiation, especially in the infra-red region of the spectrum (i.e. as IRAs) and they may be employed for this purpose in a variety of ways and in any suitable formulation for any of these uses. Uses of IRAs typically comprise any of the following 5 (although the following uses are not intended to be exhaustive): electronic devices; security applications (e.g. applying optionally colourless or weakly coloured security marks directly or indirectly to high value items such as branded articles, currency and/or cheques); additives and/or dyes for printing inks such as those inks suitable for lithographic, gravure, flexographic and/or ink jet printing; laser thermal printing, flash 10 fusion of toners; optical data storage; charge generating materials for laser thermal printing; computer to plate applications (e.g. methods which generate printed plates suitable for high volume print runs directly or indirectly from a digital image); thermal shielding; security marking, for example fuel marking; additives and/or coatings for transparent substrates (e.g. glass) such as windscreens and windows; laser welding; 15 additives to aid thermal curing (e.g. of resins) and/or any combinations of these uses.

Many compositions of Formula (1) which are particularly acceptable for use as IRAs are Ames negative.

Compounds of Formula (1) may be in the salt form as shown in the structures herein but could be in any other suitable form (e.g. an uncharged non-ionic base without 20 a quaternary nitrogen and without a counter anion A^q). Such compounds may act as a source or reservoir for the salts. The anionic counter ion (A^q) to the cyanine cations disclosed in Formula (1) may be an anion formed from any suitable species, for example an anion formed from one or more organic and/or inorganic acids and/or acid addition salts. Salts of Formula (1) comprise all IRA-effective salts that may be formed from 25 monovalent and/or multivalent acids. Salts of Formula (1) also comprise all enantiomeric salts formed with chiral anions and/or any mixtures of enantiomers of such salts (for example racemic mixtures). The present invention comprises all salts of Formula (1) and mixtures thereof, especially those which are effective IRAs.

Certain compounds of Formula (1) may exist as one or more stereoisomers, for 30 example, enantiomers, diastereoisomers, geometric isomers, tautomers, conformers and/or combinations thereof within the same moiety [e.g. the cations disclosed in Formula (I)]. The present invention comprises all stereoisomers of Formula (1) and mixtures thereof, especially those which are effective IRAs.

Certain compounds of Formula (1) may exist as one or more zwitterions, for 35 example, moieties which comprise two or more centres of ionic charge. The present invention comprises zwitterions of Formula (1) and mixtures thereof, especially those which are effective IRAs.

5 Certain compounds of Formula (1) may exist as one or more polymorphs, for example, phases, crystalline forms, amorphous forms, solid solutions, interstitial compounds and/or any mixtures thereof. The present invention comprises all polymorphs of Formula (1) and mixtures thereof, especially those which are effective IRAs.

10 Certain compounds of Formula (1) may exist in the form of one or more other complexes, for example, chelates, solvates, organometallic complexes, and/or complexes with other ligands. Such complexes may be formed between a suitable substrate in which the compound of Formula (1) and/or the substrate may act as a ligand. The substrate may comprise one or more solvents to form solvates. The complexes may be non-stoichiometric, for example if the complex is a hydrate it may comprise a hemihydrate, monohydrate and/or dihydrate. The present invention comprises all complexes of Formula (1) and mixtures thereof, especially those which are effective IRAs.

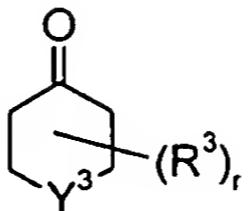
15 Certain compounds of Formula (1) may exist as one or more isotopic forms in which one or more atoms in Formula (1) comprise one or more isotopes. The natural ratios of various isotopes may be altered by suitable means, for example certain ¹²C atoms in certain compounds of Formula (1) may be substantially replaced by the less common ¹⁴C and/or ¹³C isotopes. Optionally certain isotopic forms of Formula (1) may 20 be radio-active. Certain of the isotopic forms of Formula (1) may be used as means for selective imaging in imaging devices (for example devices using X-rays, positron emission tomography and/or nuclear magnetic resonance); and/or as tools to investigate the mode of action of compounds of Formula (1) (for example as IRAs). The present invention comprises all isotopic forms of Formula (1) and mixtures thereof, especially 25 those which are effective IRAs.

30 The present invention relates to all compounds of Formula (1) even those which may not be directly effective for use as IRAs. Such compounds may nevertheless have utility in the field of the present invention for example as intermediates in the preparation and/or purification of IRA-effective compounds of Formula (1) and/or as research tools and/or diagnostic aids in relation to IRA.

Compounds of Formula (1) may be prepared by the methods described below and by other suitable methods analogous to those described in the art for similar cyanine compounds.

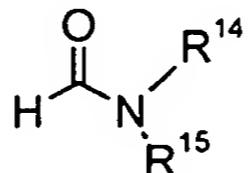
A preferred method for preparing compositions according to the present 35 invention comprises the following steps.

(a) reacting a compound of formula



where Y^3 , R^3 and r are as described herein;

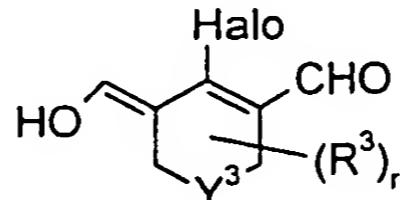
5 with a halogenating agent (optionally phosphorus oxychloride); and a compound of formula



where R^{14} and R^{15} are H or an optionally substituted C_{1-30} hydrocarbyl group;

with the proviso that at least one of R^{14} and R^{15} is aryl;

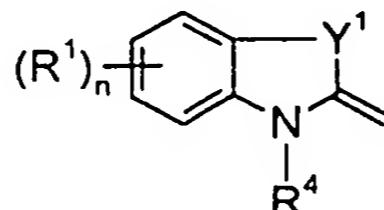
to form a compound of formula



10

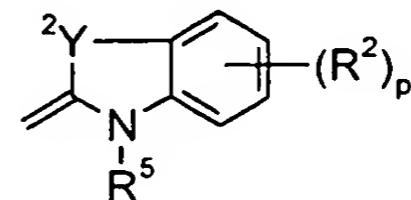
where Halo denotes a halo group and Y^3 , R^3 and r are as described herein;

(b) reacting the product from stage (a) with a nucleophile, weak acid and at least one



15 amine of formula

and/or formula



where R^1 , R^2 ,

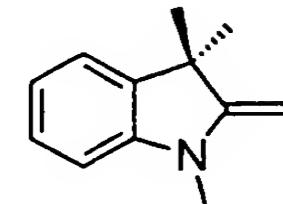
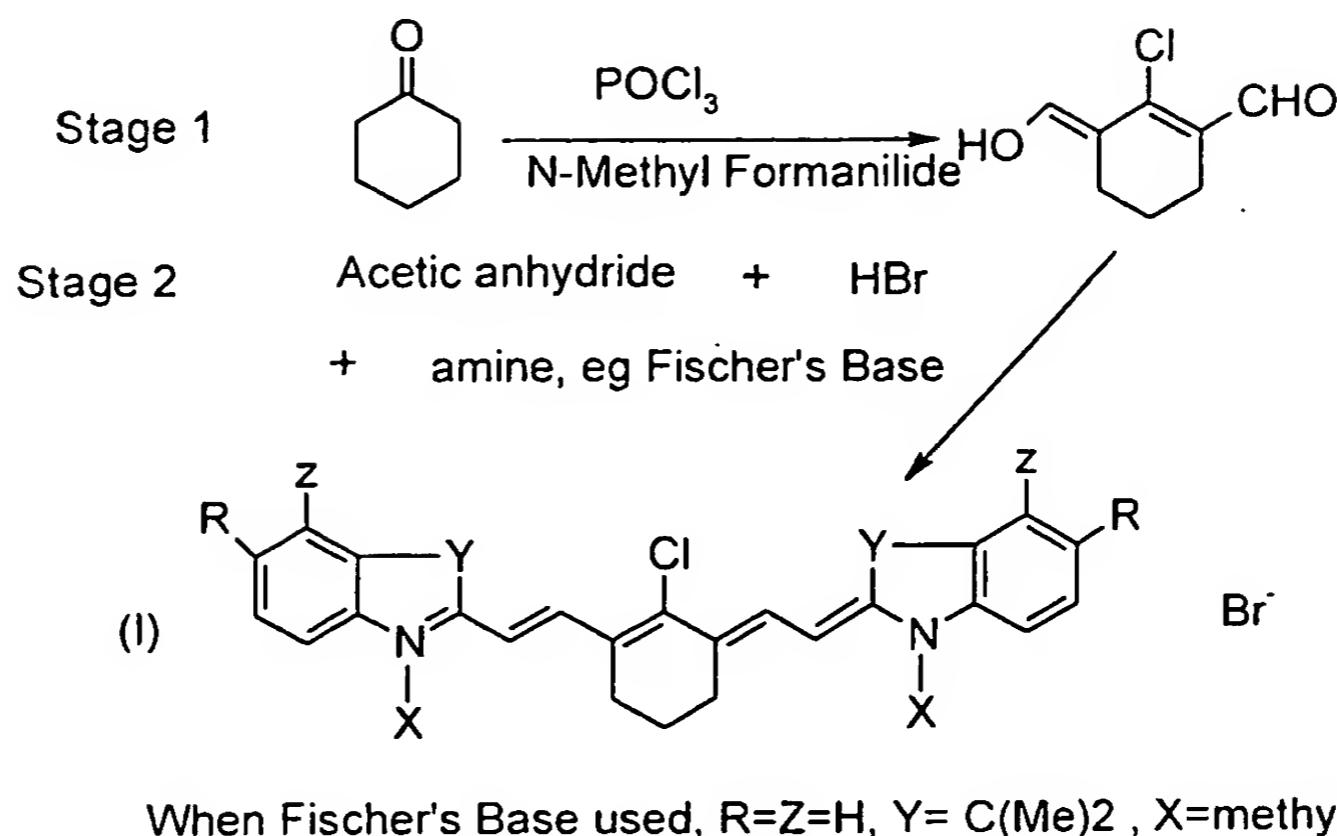
R^4 , R^5 , Y^1 , Y^2 , p and r are as described herein; to obtain a composition according to the present invention.

Preferably the nucleophile in step (b) is selected from a source of acetate and/or C_{1-4} alkanol; and optionally may be combined with tetrahydrofuran (THF) and/or a source 20 of halide or halo (e.g. hydrogen bromide). More preferably the nucleophile is selected from acetic anhydride, acetic acid, methanol, ethanol and/or mixtures thereof.

Preferably the weak acid in step (b) comprises hydrogen halide, more preferably hydrogen bromide.

Preferably, R^{14} is a C_{1-4} alkyl, most preferably a methyl group, and R^{15} is phenyl.

25 A preferred process is illustrated by the following reaction scheme.



Fischer's Base is 1,3,3-trimethyl-2-methylidene-2,3-dihydroindole; i.e.

5 The compounds of Formula (1) of particular interest are those which have a maximum absorbance peak (λ_{max}) from about 640 to about 1100 nm, preferably from about 700 nm to about 900 nm.

10 Preferably the IRAs of the present invention have a solubility of at least 1% in organic liquids. The organic liquids may be selected from aliphatic, alicyclic and aromatic hydrocarbons, alcohols, ketones, ethers, halogenated aliphatic and aromatic hydrocarbons, amides and substituted amides. Particular examples of suitable organic liquids are toluene, methanol, ethanol, 1-methoxypropanol, 2-methoxypropanol, cyclohexanone, methylethylketone, tetrahydrofuran (THF), chloroform, dichloromethane, dimethylsulphoxide and dimethylformamide.

15 Certain IRA's of Formula (1), especially those comprising sulphonate substituents, particularly alkali metal or ammonium sulphonate substituents, may be water soluble.

20 The reactions leading to the formation of the compounds of Formula 1 may be performed under conditions that have been described in the art for the use of dimethylformamide. Temperatures of from 0°C to ambient temperature, and preferably from 0-10°C may be employed. The reaction commonly takes place in the presence of one or more non-basic solvents, preferably non-basic aprotic solvents, and particularly non-basic, polar, aprotic solvents such as ethyl acetate, CH_2Cl_2 or CHCl_3 . Compositions

of Formula (1) may be isolated by known methods such as spray drying or precipitation followed by filtration.

Preferably the compositions of the present invention comprise:

- (a) from 0.01 to 30 parts of an IRA-effective compound of Formula (1); and
- 5 (b) from 70 to 99.99 parts of an IRA-compatible medium;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

10 If the IRA-compatible medium is a liquid, preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10% w/w. This allows the preparation of concentrates which may be used to prepare more dilute compositions (e.g. inks) and reduces the chance of the IRA precipitating eg from a composition comprising <10% w/w with respect to component (b) if evaporation of the liquid medium occurs during storage.

15 Preferred liquid media include water, a mixture of water and an organic solvent and an organic solvent free from water.

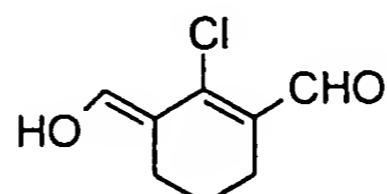
20 The IRA-compatible medium may comprise additional components, including for example resins, dispersants, binders, stabilisers and anti-oxidants. Examples of such additional components are well known in the art.

The invention is further illustrated by the following Example in which all parts and percentages are by weight unless otherwise stated. The Example describes a method of generating cyanine dyes containing a chlorocyclohexene bridging group which avoids formation of DMCC during the first stage of the reaction.

25

Example 1

1(a) - Preparation of 2-chloro-1-formyl-3-hydroxymethylenecyclohexene



30 N-methyl formanilide (515 ml) and ethyl acetate (360 ml) were stirred at 0°C to 10°C and a solution of phosphorus oxychloride (323 ml) in ethyl acetate (315 ml) was added to the mixture dropwise, followed by cyclohexanone (95 ml). The temperature of the mixture was kept below 10°C throughout the preceding step.

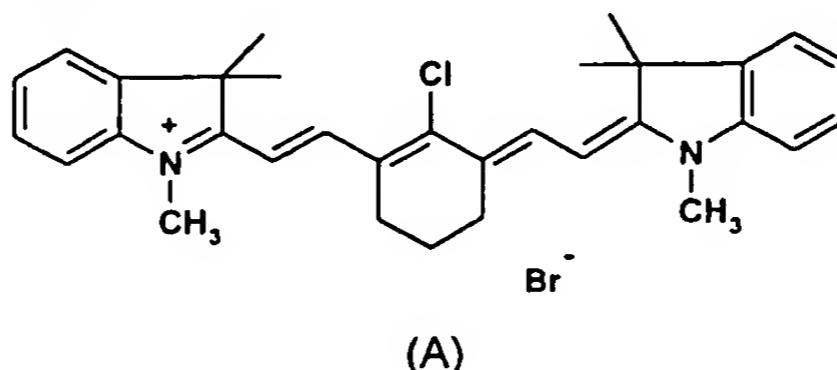
35 The reaction was stirred for four hours at room temperature, poured onto ice/water (about 3 litres) and stirred overnight. The solid was filtered, washed well with

water, dried until damp under reduced pressure and given a final wash with hexane (600ml). This resultant solid was dissolved in acetone (about 1 litre) and the solution obtained was screened and added to water (3 litres). Further water (1 litre) was added to the mixture and the resultant solid was collected by filtration washed with water and dried to give the above compound (102.5 g), micro analysis of which showed the following relative percentages of elements: C, 55.7; H, 5.1; Cl, 19.8 (compared to that calculated for $C_8H_9ClO_2$ of: C, 55.7; H, 5.2; Cl, 20.6).

The sample was found to contain less than 10ppm of phenyl methyl carbamoyl chloride and no DMCC was detected in the sample.

10

1(b) - Preparation of the cyanine dye (A)



15

The product obtained from Example 1(a) above (66.3 g) was added, at a temperature below 10°C, to a stirred solution of 1,3,3-trimethyl-2-methylidene-2,3-dihydroindole (Fischer base - 132 g) in acetic anhydride (600ml) also containing 48% HBr (96ml) and sodium acetate (62.52 g). The reaction was heated at 70° for 90 minutes, after which time it was cooled, poured onto about 4.5 litres of water and stirred overnight. The solid product obtained was collected by filtration, washed well with water and dried at 60°C, to give the title compound (167 g), which was characterised as follows $E_{max} = 253,600$ at 775nm (in methanol).

20

The NMR and mass spectroscopy data obtained was consistent with the structure.(A).

25

Comparative Example A

A(a) Preparation of 2-chloro-1-formyl-3-hydroxymethylenecyclohexene

A solution of dimethyl formamide (320ml) in dichloromethane (600ml) was cooled to a temperature below 10°C and phosphorus oxychloride (260ml) was added dropwise. Cyclohexanone (69.2 g) was added to the mixture, which was then stirred under reflux for three hours. After cooling, the reaction mixture was poured onto ice (300 g) and stirred overnight. The resulting yellow solid was collected by filtration, washed with water and dried to give the above compound (92 g), micro analysis of which showed the

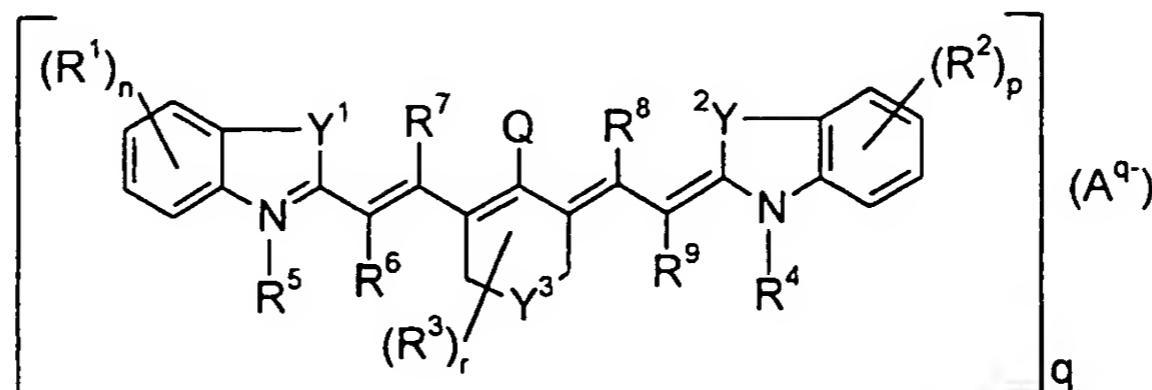
following relative percentages of elements: C, 54.6; H, 5.0; Cl, 19.9 (compared to that calculated for $C_8H_9ClO_2$ of: C, 55.7; H, 5.2; Cl, 20.6).

The sample was found to contain 4,000 ppb of dimethyl carbamoyl chloride

5 A(b) When the above material from Comparative Example A(a) (69.7g) was used to prepare the cyanine dye of structure A as given in Example 1(b) above in a manner analogous to that described in Example 1(b) herein a product (203.6g) was obtained with similar amounts of DMCC to that in the compound A(a).

CLAIMS

1. A composition of matter comprising at least one compound of Formula (1):



5

Formula (1)

where:

each R¹ to R⁹ independently represents H or an optionally substituted C₁₋₃₀hydrocarbyl group;

Q represents a substituent selected from substituents comprising at least one of carboxy, sulpho, hydroxy, alkoxy, aryloxy, amino, thio, mercapto, cyano, nitro and halo;

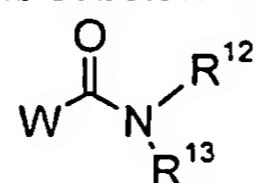
Y¹ and ²Y independently represent O, S, -NR¹⁰- and/or -C(R¹⁰)(R¹¹)-; where R¹⁰ and/or R¹¹ independently represent H or optionally substituted C₁₋₃₀hydrocarbyl;

Y³ represents -CH₂-, -CHR³- or -C(R³)₂-, or a direct bond;

A is an anion of charge (q) where q is a positive integer;

n, p and r are each independently 0 or an integer from 1 to 4;

characterised in that the composition is substantially free of compounds of Formula (II):



20

Formula (II)

wherein W represents an electron withdrawing substituent (such that when W is attached to an oxyphospho moiety the resultant species is stable) and R¹² and R¹³ are independently H or C₁₋₃₀hydrocarbyl, provided that neither R¹² nor R¹³ is aryl.

2. A composition as claimed in claim 1, which is substantially free of dimethylcarbamoyl chloride.

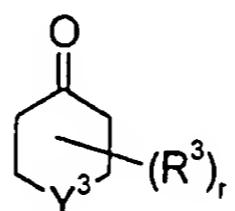
3. A composition as claimed in claim 1, which comprises no more than about 100 ppb of compound of Formula (II) with respect to compound of Formula (1).

4. A composition according to claim 3 which comprises no more than about 10ppb of compound of Formula (II) with respect to compound of Formula (1).

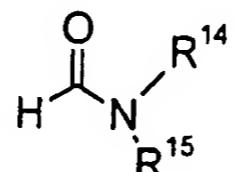
5. A composition according to either of claims 3 or 4, wherein the compound of formula (II) is dimethylcarbamoyl chloride.

10 6. A method for preparing a composition comprising a compound of Formula (1) as claimed in any preceding claims, the process comprising the steps of:

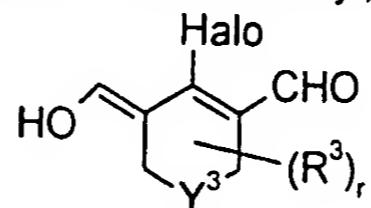
(a) reacting a compound of formula



15 where Y^3, R^3 and r are as represented in claim 1; with a halogenating agent; and a compound of formula

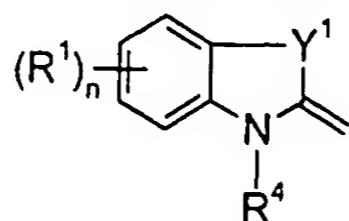


where R^14 and R^15 are H or an optionally substituted C₁₋₃₀hydrocarbyl group; with the proviso that at least one of R^14 and R^15 is aryl; to form a compound of formula



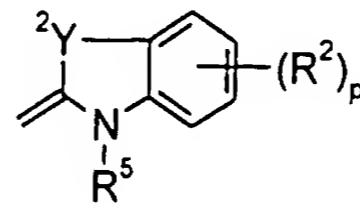
20 where Halo denotes a halo group and Y^3, R^3 and r are as represented in claim 1;

(b) reacting the product from stage (a) with a nucleophile; weak acid; and at least one



amine of: formula

and/or formula



where R^1, R^2,

R^4, R^5, Y^1, Y^2, p and r are as represented in claim 1;

to obtain a compound of Formula (I).

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7. A process according to claim 6, wherein R^14 is -CH₃ and R^15 is phenyl.

8. A composition effective for use as an infra-red absorber comprising a medium and an IRA-effective composition according to claim 1.

INTERNATIONAL SEARCH REPORT

Interr. Application No
PCT/GB 00/02778

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09B23/00 C09B23/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YU. L. SLOMINSKII ET AL: "Polymethine dyes with hydrocarbon bridges." JOURNAL OF ORGANIC CHEMISTRY OF THE USSR. (ZHURNAL ORGANICHESKOI KHIMII), vol. 14, no. 10, 1978, pages 2046-2051, XP002151108	1-5
Y	CONSULTANTS BUREAU. NEW YORK., US page 2049, Experimental, first paragraph; page 2050, paragraph 4 page 2046, last paragraph -page 2047, line 1; table 1	1-8
Y	EP 0 342 810 A (MINNESOTA MINING & MFG) 23 November 1989 (1989-11-23) page 2, line 21 - line 45; examples page 4, line 19 - line 33	1-8

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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

Date of mailing of the international search report

26 October 2000

10/11/2000

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INTERNATIONAL SEARCH REPORT

Interr. Application No
PCT/GB 00/02778

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 2 695 289 A (W.MÜLLER ET AL.) 23 November 1954 (1954-11-23) example 2 ---	1-8
A	G.A.REYNOLDS ET AL.: "stable heptamethine pyrylium dyes that absorb in the infrared" JOURNAL OF ORGANIC CHEMISTRY., vol. 42, no. 5, 1977, pages 885-888, XP002151109 EASTON US page 885, left-hand column, last paragraph -right-hand column, paragraph 1 page 886, right-hand column, paragraph 2 -----	1-8

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...information on patent family members

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PCT/GB 00/02778

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